Particles, air quality, policy and health

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Particles, Air Quality, Policy and Health [1]

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Abstract

The complexity of ambient particle size and chemical composition considerably complicates pinpointing the specific causal associations between exposure to particles and adverse human health effects, the contribution of different sources to ambient particles at different locations, and the consequent formulation of policy action to most cost-effectively reduce harm caused by airborne particles. Nevertheless, the coupling of increasingly sophisticated measurements and models of particle composition and epidemiology continue to demonstrate associations between particle components and sources (and at lower concentrations) and a wide range of adverse health outcomes. This article reviews the current approaches to source apportionment of ambient particles and the latest evidence for their health effects, and describes the current metrics, legislation and policies for the protection of public health from ambient particles. A particular focus is placed on particles in the ultrafine fraction. The review concludes with an extended evaluation of emerging challenges and future requirements in methods, metrics and policy for understanding and abating adverse health outcomes from ambient particles.

1. Introduction

Ambient airborne particles have extremely diverse physicochemical properties, sources and impacts, the latter including effects on transport, transformation and deposition of chemical species, radiative forcing and human health [1,2]. This review is restricted to the context of impacts of particles on human health only.

For the research described here it is usually only the particle phase that is being discussed, to which the word aerosol is sometimes erroneously applied (an aerosol being the combination of the particles and the gas in which they are suspended). Instead, in line with correct usage, the terminologies particle or particulate matter (abbreviated to PM), rather than aerosol, are used.

A link between poor air quality and mortality has been recognised for centuries, becoming particularly manifest as urbanisation and industrialisation intensified [3,4]. The source of air pollution was formerly dominated by widespread coal and other solid-fuel burning, plus other toxic emissions from largely unregulated industrial processes. In developed countries at least, the extent of air pollution from such sources declined markedly with the introduction of 'clean air' and 'smoke control' legislation from the mid 20th century [5], although these remain dominant sources of air pollution in some parts of the world. Since the latter part of the 20th century the coupling of increasingly sophisticated measurements of atmospheric composition and epidemiological methods has continued to reveal associations between a range of air pollutants (and at lower concentrations) and adverse health outcomes [4]. There is recognition also of the multitude of sources and complex atmospheric chemistry now contributing to poor air quality, and the wider geographic scales of influence [5].

In the contemporary context, the deleterious impact of PM on air quality and health is recognised by the World Health Organisation who publish advisory air quality guidelines for ambient concentrations of PM (and other ground-level pollutants), see Table 1 [6]. Many countries or political blocs such as the European Union have developed policies and implemented legislation to limit and reduce exposure to ambient PM. However, the complexity of ambient PM composition considerably complicates pinpointing the specific causal association between exposure to PM and adverse human health effects, the contribution of different sources to ambient PM at different locations, and the consequent formulation of policy action to most cost-effectively reduce harm caused by airborne particles.

The physical and chemical diversity of ambient PM is manifest in several ways. Particle sizes range over several orders of magnitude from linear dimensions of a few nanometre (nm) to several micrometre (μm), which strongly influences particle lifetime in the atmosphere and hence the spatial extent of their influence [2,7]. The shape and morphology of the particles are also highly variable and may comprise spheres, crystalline or irregular fragments, needles, agglomerates and dendritic entities. Individual particles may be chemically uniform, or contain chemically different core and surrounding material. An ensemble of particles may comprise similar particles or a diversity [2].

These heterogeneities are a consequence of the diverse sources of ambient PM. Primary particles are those emitted directly into the atmosphere as particles; secondary particles, or the secondary component of particles, is PM formed within the atmosphere from nucleation and condensation reactions of gas-phase species [2,8].

The major chemical constituents contributing to bulk ambient PM are well known and are summarised along with their major sources in Table 2. However, the exact composition varies markedly with particle size range, location and prevailing meteorology [8-11]. In practice, the component labelled organic carbon in Table 2 comprises hundreds or thousands of individual organic species, the majority of which are individually present at very low concentrations. Other minor and trace components include phosphate (PO_4^{3-}), and other elements, particularly metals such as Pb, Cd, Hg, Ni, Cr, Zn, Mn, emitted from a wide range of metallurgical industries [12], from vehicle engine, brake and tyre wear [13], and during combustion of impure fuel (particularly coal) and fuel and lubricating oil additives [14].

The distribution of ambient particles as a function of particle size, whether in urban or remote air, is typically characterised by three modes whose individual importance is emphasised according to whether the distribution is plotted as particle number, particle surface area, or particle volume concentration (the latter approximating to particle mass concentration if variability in particle density is small) [2], see Figure 1. The modes reflect the dominant processes giving rise to ambient airborne PM. Particles smaller than ~50 nm are termed the nucleation mode and are a newly-formed component of the particle distribution produced by homogeneous, heterogeneous or reactive condensation within the atmosphere or in the exhaust emissions from combustion processes. Nucleation mode particles are short-lived (minutes to

hours) and grow by coagulation or vapour adsorption to form the accumulation mode, which comprises particles of size from ~50 nm to 1 μm. Particles in this latter size range can remain suspended for several days since further growth is inefficient and gravitational settling and deposition slow [7]. The coarse mode particles, size >1 μm, are usually primary particles generated by mechanical abrasion processes, but may contain other constituents as a result of coagulation and condensation processes.

An important feature of the particle size distributions shown in Figure 1 is that the overwhelming majority of particles contributing to total number concentration have diameter <~0.1 μm whereas the vast majority contributing to total mass concentration have diameter >~0.1 μm. This leads to the situation in the air quality field in which particles of size 100 nm or less are termed the 'ultrafine' fraction and are quantified by their number concentration (per unit volume of air), whilst particle size distributions that include particles with diameters exceeding a μm are generally characterised by their mass concentration. It is also possible to quantify atmospheric PM by its total surface area concentration (within a stated particle size range) [15,16]. The substantial differences in properties between ultrafine particles (UFPs) and larger particles means that it is often convenient to treat them separately, as is largely done in this review.

For routine monitoring, particularly for regulatory purposes, ambient PM is quantified via the PM_{10} and $PM_{2.5}$ metrics. These are the mass concentrations of particles within a size fraction collected by samplers with inlet transmission curves that follow international sampling conventions related to 'inhalable' and 'respirable' particles, respectively [16,17]. These terms refer to the depth of penetration into the lung system, with particles in the respirable fraction capable of reaching the gas exchange surfaces of the alveoli.

The $PM_{2.5}$ sampling convention is also often called the 'fine' fraction. Particles with aerodynamic diameter between the PM_{10} and $PM_{2.5}$ sampling conventions are termed the 'coarse' fraction, $PM_{10-2.5}$ or PM_{coarse}. As stated above, particles smaller than 100 nm in diameter (the 'ultrafine' fraction) are usually quantified by number rather than mass. UFPs are of course a subset of $PM_{2.5}$ which in turn is a subset of PM_{10}.

The above is a general overview. To progress understanding on the drivers of the health effects of PM, and to devise effective strategies to reduce PM, requires detailed quantitative

information on the contributions of specific sources to human exposure to particles. The scope of this review is to summarise the latest approaches for understanding the sources contributing to ambient PM – from the perspective of its deleterious effect on air quality and human health – and the legislative approaches used to help limit those effects. The very large body of research in this wide field necessitates a focus on citation of recent specialist review articles. The review concludes with an evaluation of emerging challenges and future requirements in methods and metrics for understanding health outcomes from exposure to ambient particles, including in the policy context.

2. Measurement metrics for PM

2.1 PM_{10} and $PM_{2.5}$

The separation of particles by size for the mass-based concentration metrics PM_{10}, $PM_{2.5}$ (and occasionally PM_1) is usually accomplished by drawing the air through a cyclone or impactor designed so that particles smaller (and therefore lighter) than the specified transmission curve stay with the air flow whilst larger particles impact on to a surface [16,18]. Since separation depends on particle behaviour in an air stream, it is the aerodynamic diameter rather than the physical diameter of the particle that determines its transmission. A particle's aerodynamic diameter is the diameter of the spherical particle of unit density that has the same aerodynamic properties. In practice it is not possible to achieve a step-change in transmission through an inlet, so the value of the cut-point assigned to an inlet is the diameter for which there is 50% particle transmission.

The reference methods for quantification of PM_{10} [19] and $PM_{2.5}$ [20] involve drawing the air passing through the regulation inlet through a pre-weighed filter for a fixed time period, typically 24 h, and reweighing the filter some time later under specified conditions of temperature and relative humidity to determine the mass of PM collected. The advantage of this approach is that it is a direct measurement of mass and provides a sample that can be subjected to chemical analysis. However, it is labour intensive and provides only time-averaged data, often some considerable time after the sampling. The method is also susceptible to unintended changes in mass of both sample and filter due to adsorption or desorption of water vapour or semi-volatile gases between sampling and weighing (driven by reference

methods requirements to weigh at a specified temperature and relative humidity), or due to contamination or loss of material whilst handling [21].

Alternative methods may be used for quantification against air quality standards provided they can be shown to be equivalent to the reference method, where equivalence is tightly defined [22]. Automated, real-time quantification of PM_{10} and $PM_{2.5}$ usually uses the Tapered Element Oscillating Microbalance (TEOM®) method in which particles in the air stream (having first passed through a size-selective inlet) are collected on a small filter attached to the end of a tapered glass tube that is free to oscillate. The accumulating mass on the filter decreases the oscillation frequency of the element and this change in frequency is converted to PM mass in the air flow [23].

In the original TEOM instrument the filter was maintained at 50 ºC in order to eliminate inaccuracy associated with water condensation but this temperature also drives off some components within the PM such as ammonium nitrate and semi-volatile organic compounds [24,25]. These TEOM instruments do not demonstrate equivalence with the reference gravimetric method for either PM_{10} or $PM_{2.5}$ (under UK conditions) [26]. Recently, the FDMS® (Filter Dynamics Measurement System) has been added to the TEOM which provides two methodological improvements. First, incoming air passes through a dryer to remove water which allows the TEOM filter element to be maintained at 30 ºC, partially alleviating the loss of volatiles problem. Secondly, the incoming air is alternated in 6 minute time blocks through a purge filter which removes all PM from the sample stream before it passes over the TEOM filter. The change in mass of the TEOM filter during the 'purge' cycle yields the net effect of volatilisation and condensation processes on the mass already collected. This mass change is added to the mass recorded during the previous 'base' cycle to give the total mass of PM. A number of configurations of the FDMS-TEOM instrument have been shown in UK trials to be equivalent to the reference gravimetric methods for PM_{10} and $PM_{2.5}$, although some only after adjustments of the dryers [26]. The standard uncertainty in the FDMS-TEOM measurements were calculated in accordance with the EC Guide to equivalence [22] and, for $PM_{2.5}$, are 8.2% for model 'B', 7.25% for model 'BB', 4.4% for model 'CB' and 8.35% for model 'C' [26]. These uncertainties, along with other measurement uncertainties, have implications for assessing compliance of ambient PM concentrations with legislation [27] (see Section 6.1).

Another method to determine PM_{10} and $PM_{2.5}$ is the beta attenuation monitor (BAM) in which the attenuation of an electron beam from a radioactive beta source passing through PM accumulated on a filter is converted to a mass [28]. The attenuation of the electron beam is an indirect proxy for mass so this method is sensitive to calibration based on an assumed PM composition. The unheated BAM 1020 has been shown to meet equivalence criteria to the reference method for PM_{10} (under UK conditions) when a slope correction factor is applied [26].

2.2 Particle number concentration

Numerous methods based on aerodynamic and electrical mobility detection techniques exist to measure particle number and the detail of their working principles and limitations are given elsewhere [15,29-31]. To date, there is no methodology, instrument or detection technique that can be called the 'best' or 'standard' or that is cost-effective and robust enough for routine monitoring of number distribution over a broad size range. Instead instruments are selected for particular applications according to the type of information required, sampling frequency and size range to be measured.

Particles can be counted directly from the pulses of light scattered from them as they pass individually through a laser beam focused perpendicular to the air flow [15]. The scattering intensity as a function of scattering angle enables extraction of information on particle size [32] (using assumptions about particle morphology and optical properties). More directly, particle size can be obtained from the transit time between two closely-separated laser beams [33].

Optical scattering is only sensitive to particles larger than ~300 nm. UFPs are determined by condensation particle counter in which the air flow is drawn through a chamber super-saturated in butanol or water [34,35]. Vapour condenses onto the particle causing them to grow sufficiently large to be detected by downstream optical counter. Combination of a scanning mobility analyser with a condensation particle counter permits particle number as a function of particle size to be determined [15]. The sizing technique works by electrically charging the incoming particles and separating them according to their mobility in an electric field. The assigned size is thus the 'electrical mobility diameter' of the particle.

2.3 Black smoke

In the past, a 'black smoke' metric, based on the darkness of the particles collected on a filter paper (but actually derived from measurement of the proportion of light reflected from the filter), was widely used in Europe as the metric of ambient PM concentration [36]. There is a resurgence of interest in characterising the black carbon (or elemental carbon) component [37] since this is a good marker for the combustion-derived component of airborne particles and strongly associated with health outcomes in epidemiological studies [38]. Measurements of black carbon with modern multi-wavelength optical transmission instruments (aethalometers) offers the possibility of apportionment into different sources such as traffic and wood burning [39,40]. This is achieved by exploiting the different wavelength dependence of light absorption by PM emitted by these sources.

3. Source apportionment of PM

3.1 Bulk PM chemical analyses

Source apportionment of PM requires detailed compositional data. This may be derived from analyses of collected bulk samples of PM or from single-particle analysis [41-43]. The former approach cannot distinguish between internally and externally chemically mixed particle ensembles, but the full array of chemical analysis techniques may be applied off-line to collected samples. For particles still retained on the filter techniques include scanning electron microscopy [44], Raman spectroscopy [45], X-ray fluorescence (XRF) [46], X-ray photoelectron spectroscopy (XPS), [47,48] proton-induced X-ray emission (PIXE) [49] and instrumented neutron activation analysis (INAA) [50]. Extraction into water permits analysis of inorganic ions by ion chromatography (IC) [51]. Typical suites of analytes determined by cation and anion IC are Na^+, Mg^+, Ca^+, NH_4^+ and Cl^-, NO_2^-, NO_3^-, SO_4^{2-}, PO_4^{3-}, respectively. Extraction into water or acid is also used for elemental determination by conventional solution-phase methods such as atomic absorption spectroscopy (AAS) or inductively coupled plasma-optical emission spectroscopy (ICP-OES) [52] or -mass spectrometry (ICP-MS) [53]. Sequential extractions into multiple media have been developed [54].

A recent development is on-line instrumentation for hourly resolution of particle-phase inorganic ions, comprising a wet rotating annular denuder, a steam jet aerosol collector and parallel injection onto anion and cation chromatographs [55,56].

A major challenge remains the source apportionment of the elemental and organic carbon fractions of airborne PM [57-59], particularly the secondary organic aerosol component [59,60]. The term elemental carbon is used for the soot-like, recalcitrant carbonaceous fraction when thermal methods are used [61], whilst black carbon is generally used when optical methods are employed (Section 2.3), although recent reviews argue for more nuanced distinctions of black and brown carbon within the spectrum of light-absorbing carbon [62,63]. Difficulties of demarcating elemental and organic carbon components are well known [64]. Different combinations of temperature and gas composition, termed protocols, are used by different networks and laboratories in thermo-optical instruments for analysis of carbon, making the separation between elemental and organic carbon operationally-defined. The protocol developed recently for pan-European use is called EUSAAR II [65].

For determination of individual organic marker compounds (e.g. levoglucosan for wood burning), extraction of bulk collected samples and GC-MS or LC-MS analysis is still required. Research in this area is recently reviewed by Hays and Lavrich [66] and, for PAHs specifically, by Galarneau [67]. A thermal desorption GC×GC-MS method for determination specifically of the N-containing organic components in urban PM samples has recently been developed [68], subsequently with nitrogen-specific chemiluminescence detector [69]. Nuclear magnetic resonance (NMR), infrared spectroscopy and high-resolution mass spectrometry are increasingly applied in off-line source analysis of water-soluble organic matter [70]. UV-vis absorption spectra of water-soluble organic matter can differentiate different classes of organic compounds [71].

An emerging technique for apportioning carbonaceous PM between fossil and contemporary sources is quantification of the radioactive carbon-14 isotope using accelerator mass spectrometry [72,73]. Living material is in equilibrium with CO_2 in the atmosphere containing a known abundance of carbon-14. On death, the carbon-14 isotope decays with a half-life of 5370 years which is negligible in comparison with the age of coal, oil and natural gas fossil-fuel carbon sources. The fraction of contemporary carbon in PM carbon therefore gives the proportion of contemporary to fossil carbon in the sample. A two-step preparative combustion approach to derive the fraction contemporary carbon in the OC and EC components separately [72,73] has been applied to PM_{10} and $PM_{2.5}$ in Zurich [74], Goteborg [75] and Birmingham (UK) [76]. Even when carbon-14 determination is for total carbon (TC), rather than OC and EC

separately, combination of carbon-14 measurements with parallel chemical tracer data and modelling provides a powerful tool for apportioning TC into various sources such as primary fossil combustion sources, primary biological particles, wood burning, cooking, secondary organic carbon from fossil source, and secondary organic carbon from BVOC emissions [77-80]. These studies reveal that a large fraction of particle TC is contemporary in origin, around half on average even at urban background sites [76].

3.2 Single-particle chemical analyses

The various designs of on-line single-particle mass spectrometers have revolutionised analysis of the composition and evolution of individual (or small ensembles of) particles [43,81,82]. The common features of these instruments are an inlet that measures the size of individual incoming particles, or selects only particles of a well-defined diameter, a vaporisation and ionisation source, and a mass spectrometer [81].

Two commercial instruments are widely used in air quality research [82]. The TSI Aerosol Time-of-Flight Mass Spectrometer (ATOFMS) is a true single-particle instrument using laser ablation/ionisation which is particularly suited to characterising the evolution of particle mixing states [83-85] and the presence of refractory material such as metals [86]. The addition of an upstream thermal denuder on the ATOFMS has facilitated characterisation of particle volatility [87]. However, quantification by the ATOFMS can be limited by biases in particle inlet transmission and sizing, and in ablation and ionisation efficiency [88].

The Aerodyne Aerosol Mass Spectrometer (AMS) in its original configuration uses thermal vaporisation and electron impact ionisation, with quadrupole mass spectrometry, and is particularly suited to quantitative analysis of the non-refractory components sulphate, nitrate and organic matter. Recent AMS instrumental innovations include high-resolution time-of-flight mass spectrometers and softer ionisation techniques such as vacuum UV photoionisation, Li^+ ion, and electron attachment [89]. Attention to individual organic marker ions has permitted the organic aerosol component to be further subdivided into hydrocarbon-like organic aerosol (HOA) and oxygenated organic aerosol (OOA) [90]. From a review of AMS studies around the world, Zhang et al. [91] have demonstrated the ubiquity and dominance of OOA in atmospheric aerosol throughout the northern hemisphere. The OOA category is now further subdivided into low-volatility OOA and semi-volatile OOA [92,93]. Sophisticated

multivariate techniques – factor analysis [94], principal component analysis [95] and positive matrix factorisation [93] – are now routinely applied to AMS data to help elucidate different categories of organic PM. These data are being interpreted within a new conceptual framework for PM organic carbon, the volatility basis set, which considers the close relationship between the evolving gas-phase chemistry of semi-volatile organic compounds and their partitioning into the aerosol phase [96-98].

In general though, the above single-particle instruments cannot identify individual organic compounds. A recent development is thermal desorption-proton transfer reaction-mass spectrometry (TD-PDR-MS) which combines the strengths of the soft ionisation of the proton transfer reaction (widely used to quantify individual gas-phase organic compounds [99]) with an impactor inlet that vaporises the organic component of particles [100]. In a field campaign in the Alps, a total of 638 mass peaks in the range 18-392 Da were detected and quantified in sampled particles, and an empirical formula tentatively attributed to 464 of these compounds [101].

3.3 Source apportionment methods

Simpler source apportionment methods examine empirical or statistical relationships between receptor observations and known or surrogate sources [102]. In contrast, process-based models seek to describe mathematically all relevant processes influencing particle and precursor gas emissions, chemistry, transport and deposition between sources and receptors. These may be trajectory (or Lagrangian) models that advect individual 'parcels' of air, or Eulerian (grid) models which use a fixed coordinate system and divide the model domain into discrete cells, each of which is subject to mass balance at each time step [103]. On the urban scale, Gaussian dispersion models may be used for primary pollutants, with other approaches (e.g. computational fluid dynamics or large eddy simulation models) used in street canyons. Models often perform poorly in simulating airborne PM concentrations due to many factors including poor or missing emissions inventory data and inadequate descriptions of the atmospheric dynamics.

The 'pragmatic' mass closure method [104] seeks to reconstruct total PM mass by stoichiometric or otherwise realistic scaling of concentrations of major measured component tracers: nitrate, sulphate, chloride, EC (no scaling necessary), OC, Ca (as tracer of construction-derived dust)

and Fe (as tracer of resuspended dust). It has proved remarkably effective at giving insight into the differences in major chemical components of PM_{10}, $PM_{2.5}$ and PM_1, their variation between rural, urban background and roadside locations, and the major source contributors to days with high PM [105-107].

A powerful suite of data analysis tools specifically for atmospheric composition data is the 'openair' package developed for the R open-source modelling software by Carslaw and Ropkins [108]. These tools enable PM receptor data to be sub-divided and visualised according to many other categories, including by hour of the day and day of the week, by season, by wind direction and wind speed, or by co-pollutant concentration. These tools have been used to investigate processes affecting $PM_{2.5}$ in the UK [109,110]. The use of analysis of air-mass back trajectories as an additional tracer of PM source origin has also become popular [111].

A range of multivariate statistical approaches continue to be applied in ambient PM source apportionment. If the emission profile of all sources is known then full quantitative source apportionment is achievable through chemical mass balance (CMB) [112], subject to sufficient degrees of freedom in the data. In practice this constraint requires that the number of 'tracer' species measured at the receptor exceeds the number of sources and each source has an independent distribution of tracers. Source apportionment of carbonaceous aerosol by CMB requires extensive analysis of organic molecular markers [113], most of which are not source-specific, but which when used in combination allow sources to be distinguished [107]. However, uncertainties over source profiles require sensitivity studies [114] and, since there are no unequivocal and universally applicable molecular tracers, secondary organic aerosol is determined only as the difference between the total carbonaceous PM as measured and the sum of primary sources quantified by the CMB model.

Where information for some or all contributing sources is lacking, 'exploratory' multivariate statistical techniques such as principal component and factor analysis [115] and positive matrix factorisation [116,117] can be used to extract correlations between species concentrations at the receptor which may in turn reflect commonality of contributing sources. No *a priori* knowledge of the number of sources or source profiles is required, although emphasis of particular species in each factor aids interpretation of the likely physical sources. These methods have been particularly developed to source apportionment of air pollution [118]. An important development in the context of this review is the coupling of PM source

apportionment methods with epidemiology to try and identify sources or characteristics of PM significantly associated with adverse health outcomes. These studies are reviewed in Section 4.3.

Land-use regression models that use GIS and multiple regression to derive quantitative relationships between a dataset of pollutant observations and putative surrogate predictor variables for sources of that pollutant have become a popular approach for source apportionment and exposure estimation for chronic health epidemiology [119-122]. Variables that often turn out to be significant predictors of high concentrations of PM air pollution include distance from nearest major road, density of housing within a buffer of given radius (e.g. 250 m), and altitude (the latter in an inverse sense since higher altitude usually leads to greater wind dilution, on average). These models can now incorporate meteorological variables [123] and dispersion sub-models [124]. A criticism of this sort of work is that with sometimes dozens of possible predictor variables, the resulting regressions are rather empirical and have predictor variables that vary from one study area to another, i.e. they lack universality or transferability between locations. Another criticism is the stability in time of derived regressions; even with 'training' and 'test' datasets the regressions are inevitably tuned to the measured pollution data available so it is difficult to gauge the accuracy of the regressions for different times of the year and across different years. This shortcoming applies particularly to scenario modelling and hence to policy development.

4. PM and health effects

4.1 Current expert group summary quantifications

Knowledge of adverse health from exposure to ambient PM is derived principally from two areas of research: toxicology and epidemiology. The former is largely concerned with identification of risks and causal mechanisms, whilst the latter allows quantification of exposure-response coefficients at population or sub-population scale. Time-series epidemiological studies identify associations with short-term exposure to PM (on the day or averaged over the preceding few days), whilst cross-sectional cohort studies compare outcomes from long-term exposure of populations living in areas with different concentrations

of PM. Human challenge studies, using controlled exposures in the laboratory can also elicit valuable data, but their use is limited by ethical constraints.

Many epidemiological studies have been published, particularly of time-series design, which have investigated a range of PM metrics, populations and health end-points. Periodically, national and international agencies or expert groups review the evidence and make summary recommendations [6,8,125,126]. Exposure-response coefficients published by such reviews may then be applied to calculations of associated health and monetized burdens [127], and cost-benefit analyses of potential policy actions [128,129]. Since such expert-group recommendations must include consideration of consistency and coherence of findings across many individual studies, they are usually restricted to major health end-points (mortality and hospital admission for broad categories of aetiology) and to the general population (occasionally also stratified into children and the elderly).

A summary of the short and long-term mortality risk estimates from the most recent review by WHO (in 2005) [6] of the published literature at the time (cited in the report) are presented in Table 3. In the UK, the Committee on the Medical Effects of Air Pollution (COMEAP) publishes its own reviews and recommended coefficients. For short-term associations, COMEAP [125] noted that a summary of exposure-response coefficients from relevant studies up to 2006 (cited in the report) showed nearly all estimates for cardiovascular mortality to be in a positive direction with the majority being statistically significant. COMEAP's summary estimate for cardiovascular daily mortality was 0.9% (95% CI: 0.7–1.2%) for every 10 μg m^{-3} increase in PM_{10}, but evidence for publication bias in this estimate was noted. The association with cardiovascular hospital admissions was non-significant at 0.3% (–0.4–0.9%) per 10 μg m^{-3} of PM_{10}. COMEAP's estimate for cardiovascular mortality and daily $PM_{2.5}$ was 1.4% (95% CI: 0.7–2.2%) per 10 μg m^{-3}, with no evidence for publication bias [125].

COMEAP have also published the following recommendations for the risks for mortality associated with a 10 μg m^{-3} increase in long-term exposure to $PM_{2.5}$: all-cause mortality, 6% (95% CI: 2–11%); cardiopulmonary mortality, 9% (3–16%); and lung cancer mortality, 8% (1–16%) [126]. In the absence of major new studies on long-term effects, these latter recommendations are largely based on two seminal US-based cohort studies [130,131], particularly the American Cancer Society study [131] (Table 3).

Epidemiological studies continue to show an approximately linear increase in health risk with increasing PM exposure with no demonstrable threshold below which no effects are quantifiable [132]. However, estimates of associations at low PM concentrations have low confidence, because of a lower limit on observed PM concentrations; and within a population some individuals will be more susceptible to low concentrations of PM than others on account of, for example, pre-existing conditions or genetic make-up.

The relative magnitudes of the coefficients indicate that short-term exposure studies capture only a small amount of the overall health effects of long-term exposure to PM [133]. Conversion of a long-term risk estimate into loss of life expectancy requires application of a complex life-table approach. The estimated burden on the mortality of the UK population exposed to the anthropogenic $PM_{2.5}$ levels prevailing in 2008 for the rest of their lives is 340,000 life years lost [127]. This loss of life is an effect equivalent to 29,000 deaths at typical ages of death in 2008 in the UK, although COMEAP considers it very unlikely that this represents the number of individuals affected. Instead it anticipates that air pollution, acting together with other factors, may have made some smaller contribution to the earlier deaths of up to 200,000 people. If this number were affected, the average loss of life due to $PM_{2.5}$ would be 1.7 years each, although the actual amount would clearly vary between individuals.

The burden can also be represented as an average loss of life expectancy from birth (across all births) of 6 months [127]. This compares with estimated average loss of life expectancies in the UK of 1-3 months from road traffic accidents and 2-3 months for exposure to passive smoking [134]. However COMEAP [126] observe that a "noteworthy proportion of the total effect (of $PM_{2.5}$) is likely to appear within the first five years" so the corollary is that there will be early health gains following reductions in $PM_{2.5}$. This has been noted in the US. In a follow-up of the Harvard Six Cities Study cohort for 8 years with reduced air pollution concentration, a highly significant reduction in overall mortality was associated with decreased mean $PM_{2.5}$ [135]. A decrease of 10 $\mu g\ m^{-3}$ in the concentration of $PM_{2.5}$ has also been shown to be associated with an increase in mean ($\pm$ 1 standard error) life expectancy of 0.61 ± 0.20 year for populations in 211 counties within 51 US metropolitan areas [136]. The estimated effect of reduced exposure to pollution on life expectancy was not highly sensitive to adjustment for changes in socioeconomic, demographic, or proxy variables for the prevalence of smoking, or to the restriction of observations to relatively large counties. Reductions in air pollution accounted for as much as 15% of the overall increase in life expectancy in the study areas.

4.2 Recent epidemiology of health effects of PM

Much literature on the epidemiology of health effects of PM continues to be published. Rückerl et al. [132] recently reviewed the extent of literature on health effects of ambient PM across the spectrum of PM metrics and health variables. Authors of reviews on short and long-term exposure to PM_{10} and $PM_{2.5}$ and mortality continue to conclude that there is clear evidence of a positive association [4,133,137-141]; health effects of the ultrafine fraction of PM are covered separately in Section 5.3. Interestingly, Fischer et al. [142] report a statistically-significant upward trend in relative risk between PM_{10} and respiratory mortality between 1992 and 2006, although the authors do not exclude statistical chance, rather than increased PM toxicity, for their finding.

On the question of individual susceptibility, Sacks et al. [143] identified a diverse group of characteristics that can lead to increased risk of PM-related health effects, including life stage (i.e. children and older adults), pre-existing cardiovascular or respiratory diseases, genetic polymorphisms, and low-socioeconomic status. In terms of susceptibility to respiratory ill-health children tend to be more vulnerable than adults because their lungs are immature [144] and their defence mechanisms are still evolving [145]. Children with asthma symptoms are particularly vulnerable [144] but studies have shown reductions in lung impairment following improvements in air quality [146,147]. A review also concluded that adult lung function correlates negatively with air pollution exposure [148].

Many studies have investigated the cardiovascular effects associated with PM exposure and cardiovascular markers in relation to susceptibility to PM exposure [132,141,149,150]. In a review on PM and heart disease, Peters [151] concluded that individuals with pre-existing diseases such as chronic obstructive pulmonary disease (COPD), congestive heart disease, previous myocardial infarction or diabetes might be at increased risk of acute exacerbation on days of high PM concentration. More recent studies strengthen the evidence for diabetes and obesity as risk factors for susceptibility to vascular ill-health [152,153]. There is also evidence for the reverse, an association between long-term exposure to PM and the incidence of type 2 diabetes [154]. An emerging field of research is the association between long-term exposure to PM and decline in neural and cognitive function [155,156].

Associations between exposure to PM and pregnancy and neo-natal outcomes are reviewed by WHO [157], and others [158-160]. The WHO review states that "overall, there is evidence implicating air pollution in adverse effects on pregnancy outcomes." Results from studies on premature births, whilst pointing towards causal association [160], remain inconclusive. A time-series analysis in London found no associations between preterm births and PM_{10} in the week prior to birth [161]. Case-control studies in California showed small positive associations of pre-term birth and $PM_{2.5}$ exposure both independent of the exposure period during pregnancy [162] or during the first trimester [163]. Studies in Canada [164] and Australia [165] likewise differed in showing significant associations for PM exposure during the whole pregnancy or first trimester, respectively. Small reductions in birth weight have been noted for $PM_{2.5}$ [166,167] but not for PM_{10} [168]. Since the WHO [157] review, association between PM and post-neonatal mortality (death between 28 and 365 days after birth) has been confirmed [169-171], although a large study in London showed increased infant mortality only with SO_2 and not with PM_{10} (or other gaseous pollutants) [172].

The issue of gender differences in general in response to air pollution exposure is reviewed by Clougherty [173]. Owing to the broad differences in exposure mixes, outcomes and analytic techniques it was not possible to undertake formal meta-analysis. However it was possible to conclude that effects were generally stronger among women in adults, particularly for the elderly, and in later childhood, whilst effects were stronger among boys in early childhood. The sources of effect modification were not clear but could include differences in exposure, co-exposures and hormonal status.

4.3 Toxicity of different constituents of PM

In considering the relative toxicity of $PM_{2.5}$ versus that of PM_{10}, since the former is a significant sub-component of the latter (frequently comprising about 70%), it is hard to distinguish the impacts of the two metrics in epidemiological studies. For long-term exposure in the US American Cancer Society Study, Pope et al. [131] noted that weaker and less consistent mortality associations were observed with PM_{10} and PM_{15} than with $PM_{2.5}$. A recent time-series study in London did not reveal difference in toxicity between $PM_{2.5}$ and PM_{10} for acute exposures [174]. An alternative approach is to investigate the relative toxicities of $PM_{2.5}$ and PM_{coarse} ($PM_{10-2.5}$) which are independent metrics. Brunekreef and Forsberg [175] reviewed studies that analysed fine and coarse PM jointly and concluded that, for chronic or obstructive

pulmonary disease, asthma and respiratory admissions, PM_{coarse} has a stronger or as strong short-term effect as $PM_{2.5}$. They also noted support for an association between PM_{coarse} and cardiovascular admissions. Schwarze et al. [176] likewise concluded from a review of epidemiological and toxicological literature that PM_{coarse} has an effect that should not be neglected. A review by the USEPA [8] was less conclusive although again pointed towards evidence suggestive of associations between short-term (but not long-term) exposures to PM_{coarse} and increased health risks, with somewhat stronger evidence for associations with morbidity (especially respiratory) endpoints than for mortality.

On the other hand a systematic analysis of time-series and cohort studies using black smoke or black carbon metrics estimated that health effects are greater for these metrics than for PM_{10} or $PM_{2.5}$ and that (in time-series studies) the effect of black particles was more robust than the effect of PM mass [38]. A rapid decline in black smoke monitoring sites in the last few years means there are almost no recent time-series studies using black smoke; however, Ostro et al. [177] reported an increased positive association between daily mortality and elemental and organic carbon constituents in $PM_{2.5}$ in California, particularly for low educated people. The black smoke metric continues to be used in (retrospective) studies of long-term exposure and mortality [178-181]. Black smoke/black carbon is a good marker for traffic-related PM air pollution [36,182] so studies suggesting adverse health in association with these metrics also implicate exposure to traffic as a causal factor. A review of cardiovascular health and vehicle particulate emissions concluded that vehicular emissions are a major environmental cause of cardiovascular mortality and morbidity in the USA and suggested the promulgation of a black carbon air quality standard [183]. The literature pertaining specifically to health studies on UFP number concentration, also often a strong marker for traffic sources, is reviewed in Section 5.3.

In addition to the black smoke/black carbon studies described above, a number of other studies have sought to link either individual chemical constituents of PM, or individual sources of PM, with adverse effects on health. These include epidemiological studies using data from source apportionment techniques, animal or human exposures to concentrated ambient particles (CAPs) with parallel chemical analyses, and in vitro and in vivo toxicology experiments.

In a seminal study linking source apportionment and epidemiology, Laden et al. [184] applied rotation factor analysis to multi-element $PM_{2.5}$ concentration data in 6 eastern US cities and showed increases in daily mortality to be significantly associated with statistical factors

identified as coal burning and vehicle emission sources but not to be associated with $PM_{2.5}$ from a crustal origin. Similarly, Tsai et al. [185] applied factor analysis methods to chemical components of PM in New Jersey and reported significant associations between mortality and a number of factors assigned as oil burning, industry, vehicles, and sulphate aerosol. Sarnat et al. [186], using positive-matrix factorisation, chemical mass balance and tracers (in Atlanta, Georgia), found consistent associations between $PM_{2.5}$ from sources assigned as mobile (vehicle) and biomass burning with both cardiovascular and respiratory emergency department visits, and between sulphate-rich secondary $PM_{2.5}$ and respiratory visits. More recently, in Barcelona, Ostro et al. [187] combined positive matrix factorisation of air pollution data with case-crossover regression analysis and showed that several sources of $PM_{2.5}$, including those assigned as vehicle exhaust, fuel-oil combustion, secondary nitrate/organics, minerals, secondary sulphate/organics, and road dust had significant associations with all-cause and cardiovascular mortality. In Santiago de Chile, $PM_{2.5}$ sources assigned by factor analysis as vehicle combustion and soil were significantly associated with non-accidental mortality [188]. The literature apportioning short-term exposure to $PM_{2.5}$ into different factors and sources was recently reviewed by Stanek et al. [189]. The authors concluded that although cardiovascular effects may be associated with $PM_{2.5}$ from crustal or combustion sources, including traffic, the evidence for associations for respiratory health effects was limited, and that the collective evidence has not yet isolated factors or sources unequivocally related to specific health outcomes.

Schlesinger [190] reviewed the health impact of common inorganic components of $PM_{2.5}$: sulphate, nitrate, and acidity, and predominantly crustal-derived species phosphate, sodium, potassium, calcium, magnesium, silicon and aluminium. Although most data relate to sulphate, health outcomes have not been consistent across all epidemiology studies, and there is a lack of coherence with toxicology studies, which show biological responses only at high levels of exposure. The possibility that sulphate acts as a surrogate for the possible effects of secondary organic aerosols that might be the product of acid catalysis from SO_2 oxidation products has been noted [191]. The limited epidemiological and toxicological data for nitrate suggests little or no adverse health effects at current levels [190]. A separate review likewise concluded that evidence for a causal link between sulphate or (especially) nitrate with adverse health outcomes was weak [192]. Epidemiological studies specifically identifying crustal components of $PM_{2.5}$ suggest that they are not likely, by themselves, to produce a significant health risk, and

these components do not have unequivocal biological plausibility from toxicological studies for being significant contributors to adverse health outcomes [190].

Mauderly and Chow [193] reviewed the health effects of the organic component of PM and concluded that although some epidemiological studies have indicated associations between organic components and respiratory and cardiovascular health outcomes, current knowledge is insufficient to support a quantitative characterisation of the aggregate risk from organic components. Another review stated that soluble organic compounds appeared to be implicated in PM-induced allergy and cancer [176] but again emphasised that data from epidemiological studies were insufficient for any firm conclusions.

The consistency between epidemiological and experimental findings for specific PM-components appears most convincing for metals, which seem to be important for the development of both pulmonary and cardiovascular disease [176]. A review of the effects of metals within ambient PM identified Ni and V as particularly influential components in terms of acute cardiac function changes and excess short-term mortality [194]. The review also concluded that there is evidence that other metals in ambient PM, particularly Pb and Zn, also affect health. The utility of CAPs studies in helping to elucidate the toxicity of particular PM components has been emphasised [194,195]. Metals may also be involved in PM-induced allergic sensitization, but the epidemiological evidence for this is scarce [176].

In respect of the association between long-term exposure and lung cancer mortality reported in the US from the ACS cohort study [131], Harrison et al. [196] examined whether the association could be explained through exposure to the known chemical carcinogens As, Cr(VI), Ni and PAHs in the atmosphere (as measured in 1960 and earlier). The study found that, accounting for likely latency periods, concentrations of these chemical carcinogens could plausibly account for the carcinogenic effects of $PM_{2.5}$ exposure. However, they highlight a number of caveats, most particularly that for the chemical carcinogens to be responsible for the effects attributed to $PM_{2.5}$ the carcinogen concentrations at the time of relevant exposures would need to be correlated with the concentrations of $PM_{2.5}$ in US urban areas measured in the ACS study. It is also important to emphasise that the possibility should not be ruled out that $PM_{2.5}$ is capable of causing lung cancer independent of the presence of known carcinogens.

4.4 Mechanisms of PM toxicity

The most pervasive biological mechanistic hypothesis to explain both respiratory and cardiovascular effects is that particles depositing in the human body exert oxidative stress which, in turn, generates inflammation and a cascade of physiological processes [197-200]. In terms of respiratory impacts, oxidative stress on its own would appear to be a sufficient mechanism to provoke symptoms.

For a causal link to cardiovascular effects, it is proposed that UFPs penetrating the lung wall to the pulmonary interstitium between the lung and the bloodstream set up an inflammatory response resulting in a cascade of clotting factors leading to an increased risk of a cardiac event [201]. Subsequent additional hypotheses have led to the suggestion that UFPs can penetrate into the bloodstream causing a destabilisation of atheromous plaques on the arterial walls hence provoking a cardiac event [202]. An alternative suggestion for which there is currently less evidence is that particles depositing in the respiratory system affect the autonomic nervous system leading to a reduction in heart rate variability, which is a known risk factor for a fatal dysrhythmia [197]. Mills et al. [203] reviewed the adverse cardiovascular effects of air pollution and concluded that the main arbiter of cardiovascular effects including hospital admissions with angina, myocardial infarction and heart failure is combustion-generated nanoparticles that incorporate reactive organic and transition metal components. They argue that inhalation of this PM leads to pulmonary inflammation with secondary systemic effects or, after translocation from the lung into the circulation, to direct toxic cardiovascular effects.

A workshop of experts reported that in vitro methods for measurement of the oxidative stress potential could have an important role in the screening of toxicity of airborne PM and UFPs, although there remains a need to compare tests on a standardised samples. However, at present, no consistent trends emerge from these in vitro oxidative potential (OP) studies, nor any correlation with the results of population-based epidemiology [204]. For example, Kunzli et al. [205] examined the capacity of $PM_{2.5}$ samples to generate OH radicals in the presence of hydrogen peroxide, as well as their capacity to deplete anti-oxidants from a synthetic model of respiratory tract lining fluid, but found that PM OP varied significantly among European sampling sites, and that correlations between OP and all other characteristics of PM were low both within centres (temporal correlation) and across communities (annual mean). No robust particle size-fractionated differences in OP were observed for PM samples collected at schools in London either adjacent, or not adjacent, to busy roads [206]. On the other hand, Wessels et al.

[207] found that PM collected at high traffic locations (in the UK and Ireland) generally showed the strongest OP and that significant correlations were observed between OP and all toxicological endpoints investigated. Trace metal enrichment at the traffic polluted sites appears to have been an important factor.

A number of authors have considered the action of endotoxin adsorbed on PM as a contributor or modulator of PM toxicity, particularly through cytokine expression leading to inflammatory response, albeit predominantly via in vitro studies [208]. A review of such studies show higher endotoxin concentration in PM_{10} than $PM_{2.5}$, associated with the insoluble fraction, and in warmer seasons, but relevance for ambient PM toxicity remains contradictory [208].

5. Ultrafine particles (UFPs)

5.1 Characteristics and sources

For nearly all UFP measurements made at urban background or roadside sites, the consensus is that the sum of nucleation and Aitken modes contribute most to the total particle number concentration (PNC) [209]. For example, Charron and Harrison [210] found ~71 to 95% of total PNCs in central London in the 11 to 100 nm size range. This contribution would become even greater if particles smaller than 10 nm, which are produced through secondary formation, are taken into account. Wehner and Wiedensohler [211] found 16–24% of total PNCs in the 3–10 nm range in Leipzig (Germany) and Kumar et al. [212] reported slightly smaller contributions (4–12%) in Cambridge (UK) for the 5–10 nm size range.

As for the total particle ensemble, UFPs can be classified as ‘primary’ or ‘secondary’ which are linked mainly to the ‘Aitken and accumulation’ and ‘nucleation’ modes, respectively. In terms of size ranges for UFPs, the nucleation, Aitken and accumulation modes typically encompass 1–30, 20–100 and 30–300 nm, respectively. This modal classification is not strictly defined and researchers may use different classifications to represent various particle production mechanisms depending on the size range and sources covered [31].

Natural sources of primary atmospheric UFPs include geogenic processes (e.g. marine aerosol and volcanic particles, which both have a small UFP component) and pyrogenic processes

(forest fires, etc) [213], in addition to secondary formation via atmospheric photochemistry and condensation of semi–volatile vapours [212,214-216]. The most common atmospheric formation mechanism involves sulphuric acid nucleation, followed by condensational growth; oxidised organic compounds play a major role in the latter process [217]. Oxidation of terpenes or other organic compounds released from trees [218] and iodine oxides [219] are two other nucleation mechanisms available in natural environments. New particle formation events generally occur during high global radiation, low wind speed and low relative humidity [220]. Formation rates of 3 nm size particles are typically in the range 0.01–10, up to 100, 10^4–10^5 and 10^4–10^5 cm^{-3} s^{-1} within the atmospheric boundary layer, urban areas, coastal areas and industrial plumes, respectively [221]. Within urban and coastal areas, these formation rates can impact substantially upon ambient concentrations, and even lead to exceedences of number concentrations arising from vehicle traffic. The particle growth rate depends on the ambient temperature, coagulation, availability of condensable vapours, and deliquescence or hygroscopic particles (if humidity increases) [222], and typically varies between 1 and 20 nm h^{-1}. The smallest (0.1 nm h^{-1}) and the highest (200 nm h^{-1}) growth rates are typically reported over Antarctic and Arctic regions and coastal environments, respectively, with a typical range of 1–10 nm h^{-1} for urban environments [221].

Road vehicles are the dominant anthropogenic source of UFPs in polluted urban environments, contributing as much as 90% of total PNCs [31]. Other anthropogenic sources include combustion by–products from industries such as power plants [223], ship exhausts [224], idling, taxiing and take–off from aircraft at airports [225,226], construction, demolition or recycling of concrete [227-229], cooking [230], biomass burning, fuel combustion during gardening, waste incineration, agriculture processes, cigarette smoke and fugitive emissions [231]. Contributions to UFPs from other sources are likely to be modest compared with road vehicles in urban environments. For instance, a particle number source apportionment study by Harrison et al. [232] for Marylebone roadside in London reported about 65, 2, 5 and 18% of total PNCs from the vehicle exhaust emissions, brake dust, resuspension, and urban background sources, respectively. Likewise, a source apportionment study for urban background by Pey et al. [233] for Barcelona found 65, 1, 2, 2, 3, 24 and 3% from the vehicle exhaust emissions, mineral dust, industrial sources, sea spray, photochemical led nucleation, regional/urban background, and unaccounted sources, respectively. A recent report [234] computed the mass based contributions from different sources to the atmospheric UFPs (expressed as PM_1) in the UK as follows: combustion in energy and transformation industry (8%), combustion in

manufacturing industry (7%), industrial off–road mobile machinery (9%), passenger cars (15%), light duty vehicles (11%), heavy duty vehicles (9%), other transport (14%), production processes (15%), agriculture processes (9%) and waste (4%). However, it must be noted that the latter inventory is rough approximations based on assumptions of proportion of UFP mass for different source categories in $PM_{2.5}$ or PM_{10} inventories.

Diesel engines dominate road traffic emissions of UFPs, with average emission factors about two orders of magnitude greater than for gasoline engines [235]. Compared with diesel vehicles, emissions from spark ignited petrol vehicles are much more engine load and vehicle speed dependent [236]. For instance, the particle number emission factors for petrol cars can be in the range ~10^{12}–10^{14} veh^{-1} km^{-1} travelled depending on the speed, engine load and driving conditions, and the chassis dynamometer tests show a wide range ~10^{9}–10^{13} veh^{-1} km^{-1} travelled for a variety of engine loads applied to petrol-fuelled spark ignited engines [237]. The spark ignited petrol engines usually emit a higher proportion of smaller particles (nucleation mode), and somewhat less in the upper end of the accumulation mode where most of the particle mass resides and thus end up with lower mass emissions [236,238].

Nucleation mode particles are formed from condensation of semi-volatile vapours upon less volatile nuclei during dilution of the engine exhaust plume in the first seconds after emission [210,239]. They are nonetheless by general consensus referred to as primary emissions. Various studies have implicated sulphuric acid derived from oxidation of fuel sulphur in the nucleation process, a mechanism which has gained support from observations of a reduction in the abundance of nucleation mode particles in the atmosphere of London [240] and other cities when diesel fuel composition went from ultra-low (< 50 ppm) to zero (< 10 ppm) sulphur content. The fact that the nucleation mode particles reduce in size by evaporation as they move away from road traffic sources [241] reflects their largely semi-volatile make-up. By application of Positive Matrix Factorization (PMF) to particle size distributions measured at roadside in London, Harrison et al. [232] were able to separately quantify the normally overlapping semi-volatile particle number mode centred upon 20 nm from the graphitic solid particle mode centred upon 50 nm also emitted from road traffic (see also below). The former accounted for 38% of the on-road particle number emissions, with the latter contributing 53%. Whilst it is clear that road vehicles are currently the dominant source of UFPs in urban environments there is a need to develop inventories from a variety of exhausts and for further investigation of contributions from non–exhaust sources.

Chemical composition of UFPs in different environments is still comparatively under-studied, which is important from the perspective of source apportionment and health studies. In general terms, chemical composition is determined both during formation at the source and post–formation in the atmosphere [7]. Nucleation mode particles originating from unburned fuel and lubricating oil consist of sulphates, nitrates and organic compounds [242] due to the condensation of vapour present in the exhaust gases and nucleation (gas–to–particle conversion) in the atmosphere after rapid cooling and dilution [210,236]. Aitken mode particles are mainly made of a soot/ash core with a readily absorbed layer of volatilisable material [243] and are produced from the growth or coagulation of nucleation mode particles, and also by primary combustion sources (e.g. vehicle exhausts) in high numbers [221]. Accumulation mode particles are composed of carbonaceous agglomerates (soot and/or ash), originating mainly from the combustion of engine fuel and lube oil by diesel– or gasoline–engined vehicles [244]. These generally form in the combustion chamber, or shortly thereafter, with associated condensed organic matter [245].

The secondary particles are generally comprised of sulphuric acid, ammonium sulphates and nitrates, organic compounds and a range of trace metals. Since the chemical processes involved in the formation of secondary particles are slower, they have longer persistence in the atmosphere and consequently are more evenly distributed than primary particles but are more difficult to associate with original sources.

In a specific study, Cass et al. [246] measured UFPs in seven Southern Californian cities. The objectives were to investigate the mass–based chemical composition of particles in the 56–100 nm size range. The average values (and ranges) over all sites for organic compounds, trace metal oxides, elemental carbon, sulphate, nitrate, ammonium ion, sodium and chloride were computed as 50% (32–67%), 14% (1-26%), 8.7% (3.5-17.5%), 8.2% (1-18%), 6.8% (0-19%), 3.7% (0-9%), 0.6% (0-2%) and 0.5% (0-2%), respectively. In addition, Fe, Ti, Cr, Zn and Ce were identified. Chow and Watson [247] reviewed several studies on UFP composition. Consistent with the above results, they also concluded that organic carbon (e.g. polycyclic aromatic hydrocarbons (PAH), pesticides, phthalates, flame retardants and carboxylic acids) is the most abundant portion of UFPs in most samples. They also observed that some samples, especially those from industrial sites, were found to have high concentrations of elemental carbon (e.g. soot, black and graphitic carbon). Furthermore, K, Ca, and Fe, originating mainly

from biomass burning, combustion of oil additives and condensed vapours from industrial processes, respectively, were found to be important elements in some samples. Much of the UFPs, especially below 50 nm, was found to be semi-volatile and made of organic material such as hopanes from engine oils or condensed secondary organic aerosol such as organic acids. A few studies have also reported the abundance of PAH in UFPs. Roadside and urban background studies also reinforce these findings, stating an organic carbon to total carbon ratio of 28% for roadside particles and 51% for background particles in the 30–60 nm size range [248]. The study also found that the organic to total carbon ratio for nuclei–mode particles (i.e. those between 10–30 nm size range) was larger than for the background particles, and that OC was one of the major constituents of the nuclei–mode particles at the roadside site.

5.2 Spatial and temporal variability of UFPs

UFPs vary both spatially and temporally between the source (e.g. vehicle tailpipe) and the receptor (e.g. people travelling or living nearby the roads) depending on a number of factors such as the emission source type and strength, meteorological and dilution conditions, geographical features of an area, and transformation processes. The greatest source of ambient UFP variability derives from the reactive mixture of hot gases and particles from vehicle emissions. Unlike most gaseous pollutants, the particle size distribution continues evolving both spatially and temporally due to the dilution produced by the turbulence (atmospheric and mechanical) and the competing influences of particle transformation processes such as nucleation, coagulation, evaporation, condensation and deposition (dry and wet) [237]. Targeted efforts have also been made to relate the UFP temporal and spatial variability within the street canyons [249,250] and transport microenvironments [251-254]. These suggest that while spatial variation in UFP concentrations can exceed an order of magnitude within metres of distance, temporal variations may reach several orders of magnitude within seconds, especially immediately after the emissions close to the source [29].

With the notable recent development of instruments for measuring number and size distributions of particles >3 nm, studies are now able to capture the rapid transformations experimentally and to validate computationally or numerically the results obtained [255]. Nucleation starts playing a role in forming new particles within a second of release of exhaust emissions from the tailpipe into the atmosphere [250,256], followed by the simultaneous condensation of semi–volatile components within seconds of dilution [257]. Depending on the

ambient temperature, evaporation also occurs concurrently since the UFPs are made of volatile components and the high curvature of the smallest particles (<10 nm) favours evaporation over larger particles of the same composition (the Kelvin effect) [247]. Gases evaporated from the small particles may re–condense on larger ones, thereby shifting the distribution toward larger particle diameters [258]. These processes also counteract to neutralise each other's effects on the total PNC. For instance, emissions, nucleation and dilution increase the PNC but evaporation and deposition do the opposite; condensation does not change the PNC but contributes to increase in volume concentrations [237]. Typically, a total PNC of ~10^7 cm^{-3} is found near the exit of vehicle tailpipes which ends up with over 3 orders of magnitude dilution by the time it reaches the roadside where PNCs are generally of the order of ~10^4–10^5 cm^{-3}. Recent studies based on fast response measurements (sampling rate 10 Hz) suggest that the majority of competing influences of the transformation processes is nearly complete within about 1 s after emission due to rapid dilution in the vehicle wake [250,256,259]. These emissions can take a few tens of seconds to reach the roadside, suggesting that the majority of particle transformations are generally complete by the time particles reach the roadside.

The number and size distributions of particles continue to evolve away from the sources, but at a much slower rate due to increased time scales for various transformation processes [237]. The decay is sharpest in the first few metres distance from the road. For instance, PNCs in the 6–220 nm range near a major highway in Los Angles were found to reach half of their original values at ~30 m, and fall to the local background at ~300 m [260]. The corollary of these results is that the population living close to the roads carrying heavy traffic are expected to be exposed to higher concentrations of fresher UFPs than those residing in less trafficked areas.

Despite example research described above, the heterogeneous distributions of UFPs in various ambient environments makes dispersion modelling of ultrafine particle dynamics at different spatial scales a challenge [237]. There remains limited and partly contradicting information available on the importance of particle dynamics at different spatial scales (e.g. vehicle wake, street canyons, city or regional scales), which play an important role in the evolution of the particle size distributions. Complex flow and mixing conditions resulting from the interaction of an intricate network of streets and buildings, synoptic scale winds, surface heating and numerous pollution sources (e.g. moving traffic in urban areas) make this problem even more challenging.

It is also noted that careful design of sampling systems is essential in studies of UFPs. For instance, a significant proportion of smaller particles may be lost by diffusion and sticking to the walls in long sample inlet tubes [7]. Experiments have indicated up to 90% and 60% losses in ~13 m long sampling tubes for 5 and 10 nm particles, respectively [261]. The study showed that, despite Reynolds number indicating laminar flow in the sampling tubes, the theoretical turbulent penetration model of Hinds [7] described the experimentally estimated particle losses best, and that particle losses should be determined directly in cases when use of longer sampling tubes is unavoidable. Further apparent variability in UFP concentrations may arise from the sampling conditions and instrument detection capabilities. For example, humidity control during field measurements is important to improve the reproducibility of results. Atmospheric particles can increase up to 1.5 times in size due to hygroscopic growth at high relative humidities (80%) and hence maintaining RH below 40–50% in the sampling system is recommended for determining the physical properties of particles (see Kumar et al. [209] and references therein).

5.3 Health effects of UFPs

The large total surface area of UFPs (per unit mass), compared with the fine and coarse PM fractions, increases their role as adsorption substrates and their potential chemical reactivity [262]. Once inhaled, the very small size of UFPs allows them to go deep into the respiratory system allowing interactions between particle and lung tissue (recent research has indicated that human alveolar macrophages are incapable of removing particles <70 nm) [132,263] and potential translocation into the blood stream [263,264].

The issue of health effects of UFPs is complicated by the burgeoning field of engineered nanoparticles (ENPs) that have a similar size-based definition as ambient UFPs, but originate during the manufacture, use and disposal of nanomaterial integrated products [213,265]. ENPs have distinct physical, chemical and biological characteristics from the UFPs emitted by vehicles [262,266]. Exposure to ENPs is likely to increase in future given the ever increasing use of nanomaterial-integrated products [267,268].

It remains an open question as to which metric is best for representing the toxicity of UFPs because both generic (e.g. particle size distribution, shape, number concentrations and surface area) and more specific properties (e.g. agglomeration state, crystal structure, chemical

composition, surface chemistry, surface charge or porosity) may influence the toxicity of UFPs. While some epidemiological studies favour particle surface area as a suitable metric to quantify human exposure, others support number concentration. The former is proposed because the higher surface area to mass ratio of UFP, compared with coarser particles, permits greater contact area for adsorbed compounds to interact with biological surfaces [269]. The majority of toxicological studies demonstrate that the primary determinant of the effect of UFPs is their number and surface area and not their mass [270], calling into questioning the relevance of conventional mass-based metrics for the biological effects of UFPs [271]. On the other hand, some studies have indicated that in vitro toxicity per unit mass is largely independent of size fraction [206].

A range of reviews have provided evidence for the harmful effects of exposure to UFPs [132,263,271-273]. However, it remains clear from a recent wide-ranging review of the epidemiological evidence for health effects of particulate air pollution [132] that despite the perceived importance of UFPs as a component of PM the effects of this fraction alone have been rather little studied.

Several studies have sought to elucidate effects upon lung function. Peters et al. [274] found small but constant associations of effects upon peak expiratory flow in adult asthmatics with various measures of particle mass and number, implicating UFPs as one driver of the effects. Another panel study of adult asthmatics [275] found a link between UFP exposure and increased use of medication, while Penttinen et al. [276] failed to find an association with either respiratory symptoms or medication use.

McCreanor et al. [277] compared lung function in adult asthmatics in a busy street and an urban park finding an association of reduced lung function with exposure to UFPs, but not $PM_{2.5}$. Two other European studies [278,279] failed to find consistent associations between UFPs and lung function, as did a study in Taiwan [280]. In a time-series study of a whole urban population, Andersen et al. [281] found associations between UFP number exposure and respiratory hospital admissions which weakened after adjustment for PM_{10} or $PM_{2.5}$, which indicates that the mass metrics may have been responsible. Atkinson et al. [174] found associations for respiratory mortality and hospital admissions for particle mass metrics ($PM_{2.5}$ and PM_{10}) but not for PNC. In their review, Rückerl et al. [132] concluded that UFPs have an adverse relationship with respiratory outcomes, but that the results are not consistent.

The hypothesis advanced by Seaton et al. [201] linked UFP exposure with effects on the cardiovascular system, but epidemiology has yet to quantify the effects comprehensively. Most of the studies cited by Rückerl et al. [132] used black smoke or traffic pollution as an exposure measure, and rather few studies have measured UFPs as an exposure metric. Several studies have used heart rate variability (HRV) parameters as a measure of effect, finding both positive [282,283] and negative [284] results. Positive associations between UFP exposure and exercise-induced ST-segment depression [285], T-wave amplitude and T-wave complexity [286] and supraventricular runs [287], known risk factors for myocardial ischemia or cardiac arrhythmia, have been reported. In a time-series study of the population of London, Atkinson et al. [174] reported a significant positive association between UFP exposure and cardiovascular mortality at a lag of one day, and an almost significant association with cardiovascular hospital admissions. Stölzel et al. [288] found positive associations between UFP number concentrations and both total mortality and cardio-respiratory mortality in Erfurt, Germany, but associations with particle mass were not significant.

Rückerl et al. [132] were unable to find any studies linking UFP exposure to reproductive health outcomes. They review briefly the mechanistic aspects of UFP interaction with the human body, highlighting the high number and surface area of ambient UFP and the ability of UFP to enter the bloodstream, hence affecting organs other than the lung. However, taken together the evidence for harmful effects of UFP exposure is much stronger in the aspect of hazard (i.e. potential to cause harm) than risk (the likelihood of harm occurring). The epidemiological evidence is suggestive of adverse effects, particularly upon the cardiovascular system but does not, as yet, provide a sound case for arguing that UFP in the atmosphere presents a special risk to public health in comparison to that due to PM exposure as a whole. Clearly, further research is needed, particularly towards establishing the exposure-response coefficients that could inform the development of regulatory standards.

As discussed above, recent reports project an average loss of ~6 months in life expectancy to the UK residents due to $PM_{2.5}$ exposure and ~£20 billion per year of equivalent health costs; however such estimates are non–existent to the UFP sub-component of $PM_{2.5}$ specifically. For the first time, Kumar et al. [289] made preliminary estimates related to excess deaths in the megacity of Delhi due to exposure of vehicle–derived ambient UFP concentrations. The study applied London [174] and Erfurt [288] based exposure–response coefficients and computed ~508

and ~1888 excess deaths per million people in 2010 and 2030, respectively, under the business as usual scenario. These mortality figures were normalised for assessing relative impact of excess mortalities due to other air pollutants in Delhi. The vehicle-derived UFPs in Delhi had ~0.69 and 48 times relative mortality impact compared with the total suspended particulate matter and NO_2 exposure derived from all sources, respectively. There is a need for similar studies elsewhere but this is hindered by the lack of robust particle number emission factors and exposure-response health coefficients.

6. Policy and legislation

6.1 Current legislation and policies

Legislation to control emissions and ambient concentrations of airborne PM is formulated principally from the perspective of the protection of human health. The first such legislation was the Clean Air Acts introduced from the mid–20th century to reduce the 'smogs' produced from extensive domestic and commercial coal-burning at the time [4]. As described in Section 4, exposure-response relationships are examined through epidemiological studies. Expert groups consider the evidence and publish advice on aspects such as concentration-response coefficients, thresholds and ambient concentration limits. The latter may subsequently be incorporated into legislation as ambient air quality standards. Table 4 lists the UK, EU and USA standards for ambient particles as defined through the PM_{10} and $PM_{2.5}$ metrics. The protocols that prescribe the measurement of PM_{10} and $PM_{2.5}$ have been described in Section 2. The EU also has air quality standards for the following specified chemicals in particles: benzo(a)pyrene, As, Cd, Ni and Hg (Table 5).

The first of the contemporary standards for PM were developed during the 1990s. In the EU, these were based on the PM_{10} metric with focus principally on limiting exceedences of a 24-h average concentration as prescribed in the First Daughter Directive [290] of the Air Quality Framework Directive [291]. An annual mean limit value was also included but in practice this was less stringent than the 24-h limit value. EU member states transpose the Directive requirements into their own legislation. In the UK, there is an obligation on local authorities to develop Air Quality Action Plans in pursuit of the objectives where they are, or are predicted to be, exceeded.

The focus of legislation on fixed concentration standards leads to policy action that emphasises identification and mitigation of pollution 'hot spots' without regard to the extent of population affected. The mounting evidence that the fine fraction of PM may be more harmful, and that long-term concentrations have greater health (and associated cost) burden than short-term peaks, has led to a change in focus in ambient PM legislation. The EU Directive (2008/50/EC) on ambient air and cleaner air for Europe [292], which came into force on 11 June 2008, merged the previous EU legislation and introduced standards for $PM_{2.5}$, including the concept of a population-weighted reduction in 3-year annual $PM_{2.5}$ at urban background locations. The latter is in recognition of the absence of evidence for a threshold concentration for adverse health effects from $PM_{2.5}$ and consequently that greater gain in health overall can be achieved by focusing on policy that leads to reductions in pollutant concentrations across the greatest extent of population, irrespective of the absolute concentrations relative to some arbitrary value. Note, however, that this also assumes that all components of $PM_{2.5}$ are equally toxic.

The 2008 EU Directive air quality standards for $PM_{2.5}$ have two components: a limit value to ensure that extreme hot spots exposures are not ignored, and a target to deliver a specified reduction between 2010 and 2020 in population-weighted exposure in each member state [292]. The percentage reduction required depends on the 3-year average population-weighted $PM_{2.5}$ concentration for the period 2009-2011 (Table 6). The Directive specifies the spatial density, location characteristics and types of $PM_{2.5}$ monitors required to calculate a member state's population-weighted exposure. De Leeuw and Horalek [293] compared sensitivity cases in which the limit value was met everywhere or the exposure-reduction target had been met by all countries. They concluded that the exposure-reduction approach results in a larger reduction in the burden of disease than meeting the limit values. A current concern, however, is that uncertainties in different aspects of quantifying the average exposure indicator (e.g. individual analyser measurement uncertainty, combination of many analyser measurements into the AEI, effects of analyser maintenance, replacement and relocation, meteorologically-driven inter-annual variability) combine to give total uncertainty in AEI comparable to the target reduction [27]. While this study highlights an important issue, the matter requires greater scrutiny, including a more detailed statistical analysis of available data. Furthermore, if evidence mounts for differential toxicity of particles then abatement measures need to be more targeted.

The second legislative approach to reduce exposure to PM focuses on controlling emissions of primary PM and the precursors gases contributing to secondary PM (SO_2, NO_x, VOC and NH_3, and to some extent CH_4 also). A myriad of such legislation exists. The use of supra-national legislation to control emissions is appropriate because of the considerable transboundary transport of PM and its precursors [294,295]. The UN Economic Commission for Europe Convention on Long-range Transboundary Air Pollution provides an international policy framework. The 1999 'multi-effect' or 'Gothenburg' Protocol to Abate, Acidification, Eutrophication and Ground Level Ozone [296], ratified by countries across Europe, North America and northern Asia, sets national emissions ceilings for SO_2, NO_x, VOCs and NH_3. In the EU, the requirements of this protocol are incorporated within the National Emission Ceilings Directive (2001/81/EC) [297] which set member state emission targets to be attained by the end of 2010. The UNECE Protocol is currently being revised with new targets to be set for 2020 for the four pollutants already regulated plus primary emissions of $PM_{2.5}$.

Other EU legislation relevant to emissions controls includes the Large Combustion Plant Directive (2001/80/EC) [298], which applies to combustion plants with rated thermal input of ≥50 MWth, the Integrated Pollution Prevention and Control Directive (2008/1/EC) [299], which applies to all industrial installations (including some agricultural processes), the Solvent Emissions Directive (1999/13/EC) [300] and the Waste Incineration Directive (2000/76/EC) [301]. These Directives have been consolidated into a new Industrial Emissions Directive (2010/75/EU) [302] which entered into force in 2011, to be transposed into member state regulations by January 2013.

Emissions from transport are also highly regulated in many countries. The EU has a phased series of emission 'type approval' standards for light and heavy-duty vehicles, which has currently reached the 'Euro 6' standard – see Section 6.2 below. Emissions are also controlled through in-service vehicle tests and legislation on fuel quality. However, recent evidence from ambient monitoring indicates that emissions limits met in diesel engine test-cycles have not translated to on-road driving, for NO_x at least [303]. Emissions from non-road mobile machinery in the EU have their own Directive (97/68/EC) [304] (plus later amendments), and covers equipment such as agricultural and forest tractors, industrial drilling rigs, compressors, bulldozers, non-road trucks, excavators, forklift trucks, snow ploughs, road maintenance equipment, mobile cranes, and ground support equipment at airports. Emissions standards

under later amendments of the Directive also include railway locomotive engines and engines used for inland waterway vessels [305,306].

Emissions from shipping are controlled under the International Convention for the Prevention of Pollution from Ships (MARPOL). A 2008 revision sets out increasingly stringent controls on shipping SO_2 and NO_x emissions between 2010 and 2020 [307]. The International Civil Aviation Organisation through its Committee on Aviation Environmental Protection sets emission standards for current and new aircraft engines; engines certified from 2008 have to meet the CAEP/6 standards [308]. The particle metric used is, however, rather crude.

6.2 Legislation and policy pertaining to UFPs

The only legislation pertaining to UFPs specifically (in Europe) is via the Euro 5 and Euro 6 vehicle emission standards [309]. These regulations are the first of this kind to control UFP emissions for solid particles >23 nm diameter. The lower particle cut–off is to exclude semi-volatile nucleation mode particles in order to enhance the prospects of repeatability in measurements. It also minimises the effects of both small volatile particles and diffusion losses during sampling [261].

The lower cut-off set by the Euro standards means that more than 30% of the smallest UFPs in urban environments may not be included [211]. Arguably, a future regulatory framework should consider this smaller size range also. Furthermore, whilst these regulations limit the emissions of UFPs to the environment from one key source, they do not in themselves regulate the exposure of the public to UFPs. Ambient air quality standards for UFPs currently do not exist anywhere in the world, but merit consideration.

However, development of any future legislation on emissions or ambient levels of UFPs first requires a number of technical challenges to be overcome [31,209,213]. These are numerous but the following are some of the key issues that require attention.

First, there is a lack of standardised instrumentation and sampling protocols for UFP measurement. Recent studies [310,311] have found notable differences in particle number concentrations and size distributions when measured simultaneously using a number of widely used instruments in identical sampling conditions. Instruments may quantify particle size as

either an electrical mobility or aerodynamic diameter and different sizing principles can lead to significant differences for non-spherical particles (i.e. most of the accumulation mode particles). Furthermore, measurements can also be significantly affected by particle shape and density, even for instruments working on the same detection technique. For coping with the issue of reproducibility of measured data, ready–to–use algorithms are therefore desirable to correct the data from different instruments, but are unlikely to accommodate the complexity caused by different physical principles of measurement.

A consensus is not yet reached on a metric for ambient UFPs. A successful deployment of a particle number metric in Euro standards for vehicles gives this metric an edge over others such as the surface area or chemical composition, though the matter remains open to debate.

Paucity of exposure–response relationships is another area for continued research before a consensus on limits to exposure to ambient UFPs can be recommended. Crucial to defining a limit value is the averaging period to be used. While background PNCs may be expected to remain fairly stable in the absence of nucleation bursts, PNCs within an urban area show a remarkable variation, both temporally and spatially [241]. For instance, 24 h, 1 h and 1 s average concentrations in the close proximity of sources in an urban area can be up to 1, 2 and 4 orders of magnitude larger, respectively, than the equivalent in the urban background [213,249]. Nucleation bursts can also cause very rapid temporal variations in PNC [217]. This means that UFP mitigation policies would need to target a decrease in UFPs in stated spatial or temporal averaging domains, which is clearly a challenging task [312]. This temporal and spatial variability of UFPs is very much greater than for $PM_{2.5}$ or PM_{10}.

7. Emerging challenges and future requirements

7.1 Health outcomes, metrics and methods

For health effects studies, an important need remains accurate exposure data, whether that is to total PM or to individual chemical components or sources [313]. This is particularly the case for long-term studies where within-city small-scale spatial variations in exposure may exceed between-city contrasts [120]. The issue of the extent of error in epidemiological studies from variability and misclassification of personal exposure is well known but largely unresolved [314].

Development of small and portable sensors for PM or particle number that can be widely distributed and networked may herald a new era in micro-environment and personal exposure characterisation [315-317]. At the other end of the spatial extreme, a developing research field is spatially-resolved measurement of particles over wide areas via satellite remote sensing [318,319].

In terms of health outcome, there has been most focus on mortality and on short-term exposures. More studies on effects of chronic exposure to PM are needed [132]. These studies are complex to analyse if retrospective, and expensive and have long delay to results if prospective. However they are urgently needed because chronic effect studies indicate that long-term exposure to PM dominates population health burden [133] and results from these studies form the core of current air quality standard setting. Effects of exposure to PM on reproduction and neuropathology are under-studied [132].

As more epidemiological and toxicological studies are performed consistency and coherency between the two types of studies should continue to develop [176,320,321]. There is an important need to develop simple laboratory-based *in vitro* screening tests for relative toxicity of ambient particles and source-related samples. While such tests exist currently, they are not adequately inter-compared, and there is wholly insufficient knowledge of how their outcomes relate to toxic effects in human populations [204].

In terms of PM metric, the overwhelming focus has been on the mass concentration metrics PM_{10}, $PM_{2.5}$ and to a much lesser extent PM_{coarse}. Insufficient attention has been paid to the coarse particle fraction, despite numerous studies indicating associations with adverse effects. The fact that such associations are often less clearly observed than for the fine particle fraction may be the result of greater variability [322] and hence increased exposure misclassification in epidemiological studies, which tends to bias results towards the null. There is also an urgent need for more epidemiological studies on the health effects of UFPs. Using measured particle size distributions as the basis for calculating regional lung dose, PM_{10} has been found to be a good predictor of mass dose in all regions of the lung but a poor predictor of particle surface area and number dose. Similarly, measurements of PNC do not well predict mass dose [323]. Consequently, to quantify health effects of both particle mass and number requires separate measurement of both.

As more data on chemically-speciated PM becomes available focus will shift to examining the associations with individual chemical components or, via source apportionment techniques, to individual types or sources of PM. However, these methods also have important limitations, including failure to identify specific sources, misidentification from co-mingled source factors and inconsistency or unreasonableness of results from the same locations using different factor techniques [324]. This can result in part from a failure to distinguish between statistically-based factors and actual sources. In addition, as speciated measurements and source apportionment and other modelling techniques become more sophisticated it should be possible to start addressing quantitatively another important issue: the independence or not in effects from multipollutant exposures [325].

A prominent emerging aspect pertaining to UFPs is the possible intrusion of airborne ENPs such as carbon nanotubes, titanium oxides, silver nanoparticles [268]. The increasing demand and manufacture of nanotechnology-integrated products, due to their novel properties and applications [267], is likely to lead to increased release of ENPs into the environment throughout the life-cycle of manufacture, use and disposal [326]. Release of ENPs in indoor commercial and research units during manufacture and handling are currently being dealt with as a high priority worldwide. However, studies quantifying number concentrations, size distributions and impacts of ENP in the outdoor environment are few. Because of their distinct physical and chemical characteristics, ENPs are likely to be non–volatile and persist longer in the atmosphere. The impact on human health requires urgent consideration but research in this area is still in its infancy [326]. Future research requirements include accurate physicochemical characterisation of ENPs, their apportionment from the ambient UFPs, and exposure–response functions for different types of nanomaterials [213].

7.2 The policy context

Airborne particulate matter covers more than four decades of size, and has highly diverse and spatially variable chemical composition. Regulating it as PM_{10} is implicitly treating it as a single pollutant, yet it seems implausible that different size fractions and chemical components contribute equally to toxicity. While the separate regulation of $PM_{2.5}$ is an acknowledgement of different toxicity, there are cogent arguments that once research has cast more light on the relative toxicity of different components, it will be more cost-effective to focus regulations upon the most toxic constituents, or the emission sources primarily responsible for them. At

present, the knowledge base lacks the consistency and coherence necessary to make such judgements with confidence.

An immediate concern, in the EU at least, is to measure $PM_{2.5}$ with sufficient accuracy and precision to determine, with confidence, the compliance of individual states to the $PM_{2.5}$ population-weighted exposure reduction targets [27] set in current legislation [292]. Accurate and precise measurement of total particle mass, particle number, and chemical components, remains a major challenge, particularly in the context of defining legislation for ambient particles.

Results emerging from health studies suggest an important negative impact from traffic-related emissions [38,321] and consequently that consideration be given to metrics based on black (or elemental) carbon and/or to UFP number concentrations which are better markers of this source than $PM_{2.5}$ [37,38,183]. In any event, increasing sophistication of speciated measurements and source apportionment techniques should drive legislation towards a more source-based and multi-pollutant framework [321,325].

UFP number concentrations are currently not monitored routinely as part of conventional air pollution monitoring. Such measurements should be encouraged better to quantify exposure to UFP, to understand relationships with sources and meteorology, and to help validate UFP dispersion models and emission inventories [237]. An enhanced measurement base would also support the development of more powerful epidemiological studies. This could include regular monitoring of UFP alongside the routinely monitored gaseous pollutants as a part of national networks. However, a number of technical constraints need to be overcome, including the appropriate measurement locations and techniques, before any nationwide routine monitoring is proposed for policy purposes. For instance, the strong spatial and temporal variability of UFPs (see Section 5.2), in addition to the fact that routine monitoring stations are usually situated some distance away from the source, and that the smaller particles (especially the freshly emitted nucleation mode) are highly volatile in nature [241], makes it difficult to decide on a representative measurement location. Moreover, there are currently no standard guidelines on the use of ambient UFP measurement instruments [209]. This and the findings from instrument comparison exercises [310,311] that have shown notable differences in measured outputs of total particle number concentrations using different instruments in identical conditions, leave challenging questions on the selection of appropriate UFP instruments for

routine monitoring and the lower cut–off size for any future regulations on a particle number basis (see also Section 6.2). More studies of the spatial variability of UFP number counts are a pre-requisite to network design.

Organic carbon is an important component of PM [76,91]. Whilst there is currently insufficient evidence for adverse health effects from this fraction specifically [193], legislative requirements to reduce total PM mass will likely necessitate reduction in PM organic carbon in addition to reductions in other components of PM. An assumption that the biogenic secondary organic component of organic carbon is natural and therefore not amenable to controls has been shown to be misguided [327]. Anthropogenic pollution facilitates transformation of naturally emitted VOCs to the particle phase OC, and modelling for the eastern US has shown that more than 50% of biogenic SOC production can be removed by control of anthropogenic emissions of other pollutants such as NO_x, VOC and primary $PM_{2.5}$ [327].

In developing policy actions it is important that policy-makers recognise where there are instances of win-wins or won-lose between policies formulated to improve PM air quality on the one hand and within other arenas, in particular in mitigation of climate change, on the other. The potential overlaps between air quality and climate change are myriad and complex [328,329]. An example win-win is reduction of black carbon particles benefits both air quality and climate change [330,331]; an example win-lose is where a switch to biomass burning as a means to reduce fossil CO_2 emissions leads to greater emissions of particles. A full life-cycle and cost-benefit approach is essential.

To meet the reduction targets for carbon emissions, requirements for the use of renewable fuels (e.g. biofuels) and stringent emission standards are being applied in Europe and elsewhere. While the use of biofuels in vehicles has been found to decrease CO, CO_2 and particle mass emissions, PNCs have been observed to increase at many locations. One explanation is that combustion of biofuel in engines reduces the accumulation mode solid particles which reduces the surface area of solid particles for condensation and hence promotes the nucleation mode [332]. Another mitigation measure involves use of exhaust treatment devices such as diesel particulate filters (DPFs). One such example is the retrofitting of DPFs from January 2012 in London for diesel vehicles not complying with the Euro 4 emission standard in the Low Emission Zone. The use of DPFs has been found to decrease particle number emissions by up to two orders of magnitude in comparison with ‘untreated’ diesel vehicles [333],

besides effectively removing the solid particles (i.e. particle mass) in the accumulation mode [271]. However, the use of DPFs may lead to regeneration of UFPs by emitting volatile precursors which can facilitate the formation of large numbers of particles in nucleation mode under high load conditions [271]. This also raises the question of effectiveness of exhaust treatment devices in biofuelled vehicles for reducing PNCs. On the other hand, the steep reduction in PNCs at UK sites following the introduction of zero-sulphur diesel [240] provides an example of an unplanned but beneficial effect of policy intervention designed to facilitate the introduction of advanced emission abatement devices.

Finally, it is important that policies aimed at reducing levels of ambient PM are evaluated post hoc for their efficacy in reducing concentrations and improving population health outcomes [334]. There is observational evidence that whilst levels of PM in Europe have declined with time, the decline has not been as great as emissions of primary particles and precursor gases would imply [335]. This may reflect poor knowledge of sources which are difficult to quantify (e.g. wood smoke, non-exhaust particles from traffic), non-linearity of precursor-secondary aerosol relationships (as, for example, for sulphate [336]), changes in weather patterns, or a combination of factors. Nevertheless, significant reductions in mortality and gains in life expectancy have been recorded for reductions in mean $PM_{2.5}$ concentrations in the US [135,136] and for reductions in black smoke in Dublin following a coal sales ban [337]. The introduction in London (from 2008) of the world's largest Low Emission Zone is providing an unprecedented opportunity for the prospective evaluation of policies aimed at reducing emissions from traffic sources, in particular, on ambient PM concentrations and composition, and on the health of the London population [338,339].

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Table 1:
Current World Health Organisation advisory air quality guidelines for PM_{10} and $PM_{2.5}$ [6]. Interim targets towards these guidelines are also specified by the WHO.

PM metric	Annual mean	24-hour mean [a]
PM_{10}	20 µg m^{-3}	50 µg m^{-3}
$PM_{2.5}$	10 µg m^{-3}	25 µg m^{-3}

[a] as 99th percentile (3 days exceedance/year).

Table 2: Major constituents of airborne PM and their principal sources [8,10].

Component	Notes
Sulphate (SO_4^{2-})	Present mainly as a secondary ammonium sulphate component ($(NH_4)_2SO_4$) from atmospheric oxidation of SO_2 followed by reaction with NH_3 gas derived mainly from agricultural sources, although there may be a small primary component derived from emissions of sea-salt particles or mineral matter such as gypsum.
Nitrate (NO_3^-)	A secondary component normally present as ammonium nitrate (NH_4NO_3), which results from the neutralisation by NH_3 of HNO_3 vapour derived from oxidation of NO_x emissions, or as sodium nitrate ($NaNO_3$) due to displacement of hydrogen chloride from NaCl by HNO_3 vapour.
Ammonium (NH_4^+)	Generally present in the form of $(NH_4)_2SO_4$ or NH_4NO_3 from NH_3 emissions
Sodium (Na^+) and chloride (Cl^-) ions	From primary emissions of sea-salt particles
Elemental carbon	Black, graphitic carbon formed during the high-temperature combustion of fossil and contemporary biomass fuels.
Organic carbon	Carbon in the form of organic compounds, either primary, from automotive or industrial sources, or secondary, from the oxidation of volatile organic compounds (VOC).
Mineral material	Crustal materials are rich in elements such as Al, Si, Fe and Ca. These are present in primary coarse dusts that arise from, for example, wind-driven entrainment of soil and mineral material, quarrying, construction and demolition.
Water	Water-soluble components, especially $(NH_4)_2SO_4$, NH_4NO_3 and NaCl, take up water from the atmosphere at high relative humidity, turning from crystalline solids into liquid droplets.

Table 3: Summary mortality risk estimates for exposure to PM from the most recent review by WHO [6].

PM metric	**Outcome**	**Data source**	**Estimate (95% confidence interval)**
PM_{10}	Daily mortality (all-cause)	WHO meta-analysis [340]	0.6% (0.4 – 0.8%) per 10 µg m^{-3}
PM_{10}	Daily mortality (respiratory)	WHO meta-analysis [340]	1.3% (0.5 – 2.09%) per 10 µg m^{-3}
PM_{10}	Daily mortality (cardiovascular)	WHO meta-analysis [340]	0.9% (0.5 – 1.3%) per 10 µg m^{-3}
PM_{10}	Daily mortality (all-causes)	Health Effects Institute NMMAPS[a] reanalysis [341]	0.21% (0.09 – 0.33%) per 10 µg m^{-3}
PM_{10}	Daily mortality (cardiovascular)	Health Effects Institute NMMAPS[a] reanalysis [341]	0.31% (0.13 – 0.49%) per 10 µg m^{-3}
$PM_{2.5}$	Long-term mortality (all-cause)	ACS CPS II[b] 1979 – 1983 [131]	4% (1 – 8%) per 10 µg m^{-3}
$PM_{2.5}$	Long-term mortality (cardiopulmonary)	ACS CPS II[b] 1979 – 1983 [131]	6% (2 – 10%) per 10 µg m^{-3}

[a] NMMAPS = National Morbidity, Mortality and Air Pollution Study
[b] ACS SPS II = American Cancer Society Cancer Prevention Study II

Table 4: Current legislated ambient air quality standards for PM in the UK, EU and USA.

Legislative region	Metric	Averaging period	Standard	To be achieved by
UK (excluding Scotland)	PM_{10}	24-hour mean	Objective[a] of 50 µg m^{-3} not to be exceeded more than 35 times a year	31 Dec 2004
		Annual mean	Objective of 40 µg m^{-3}	31 Dec 2004
	$PM_{2.5}$	Annual mean	Objective of 25 µg m^{-3}	2020
		3 year running annual mean	Target[b] of 15% reduction in concentrations measured across urban background sites	Between 2010 and 2020
Scotland	PM_{10}	24-hour mean	Objective of 50 µg m^{-3} not to be exceeded more than 7 times a year	31 Dec 2010
		Annual mean	Objective of 18 µg m^{-3}	31 Dec 2010
	$PM_{2.5}$	Annual mean	Objective of 12 µg m^{-3}	2020
		3 year running annual mean	Target of 15% reduction in concentrations measured across urban background sites	Between 2010 and 2020
EU	PM_{10}	24-hour mean	Limit value[c] of 50 µg m^{-3} not to be exceeded more than 35 times a year	1 Jan 2005
		Annual mean	Limit value of 40 µg m^{-3}	1 Jan 2005
	$PM_{2.5}$	Annual mean	Target value[b] of 25 µg m^{-3}	2010
		Annual mean	Limit value of 25 µg m^{-3}	2015
		Annual mean	Stage 2 indicative limit value[d] of 20 µg m^{-3}	2020
		3 year Average Exposure Indicator (AEI)	Exposure reduction target relative to the AEI depending on the 2010 value of the 3 year AEI (ranging from a 0% to a 20% reduction)[e]	Between 2010 and 2020
		3 year Average Exposure Indicator (AEI)	Exposure concentration obligation of 20 µg m^{-3}	2015
USA	PM_{10}	24-hour mean	150 µg m^{-3} not to be exceeded more than once per year averaged over 3 years	In force
	$PM_{2.5}$	24-hour mean	35 µg m^{-3} as 98th percentile averaged over 3 years	In force
		Annual mean	15 µg m^{-3}	In force

[a] A UK objective includes the target date on which exceedences of the standard must not exceed the specified number.

[b] Targets and target values are set out in the same way as objectives and limit values, and are to be attained where possible by taking all necessary measures not entailing disproportionate costs, but not legally binding.

[c] Limit values are legally binding on EU member states.

[d] Subject to review in light of future information on health effects and technical feasibility of implementation.

[e] See text for further explanation

Table 5: European Union target values for particle-bound chemical species, as specified in Directive 2004/107/EC [342].

Pollutant	Measured as	EU Target Value	Date to be achieved
Benzo(a)pyrene [a] (in PM_{10} fraction)	Annual mean	1 ng m^{-3}	31st December 2012
As (in PM_{10} fraction)	Annual mean	6 ng m^{-3}	31st December 2012
Cd (in PM_{10} fraction)	Annual mean	5 ng m^{-3}	31st December 2012
Ni (in PM_{10} fraction)	Annual mean	20 ng m^{-3}	31st December 2012
Hg (total) [b]	Annual mean	No target value specified, but 50 ng m^{-3} is a guideline	

[a] as a measure of total PAH
[b] includes Hg in particle phase

Table 6: European Union national reduction targets in $PM_{2.5}$ Average Exposure Indicator (AEI) according to the AEI value in 2010, as specified in Directive 2008/50/EC [292].

2010 AEI concentration (µg m^{-3})	2020 target AEI reduction (%)
≤ 8.5	0%
>8.5 – <13	10%
13 – <18	15%
18 – <22	20%
≥ 22	All appropriate measures to achieve 18 µg m^{-3}

Figure 1: A typical ambient particle distribution as a function of particle size expressed by particle number, surface area, and volume. The latter is equivalent to a mass distribution when variation in particle density is small. Vertical scaling is individual to each panel.